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(54) Description: Process for production of Bisphenol-A-Polycarbonate according to the melting transesterification process.

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Process for Production of Bisphenol-A-Polycarbonate According to the Melting Transesterification Process

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The well known transesterification process for production of high-molecular Bisphenol-A-Polycarbonate consists of heating the Diester of Carbonic Acid, the Diphenylcarbonate, along with the aromatic Dihydroxy campound, the Bisphenol A, if required in the presence of catalysts, to temperatures between 50^0 C and 350^0 C under reduced pressure. (For transesterification process see for example US-PS 3 275 601 and US-PS 2 946 766).

Disadvantageous for the constancy of quality in quality of the Polycarbonate is the hitherto common manner of loading the raw material in this process: Crystallized Bisphenol A gets melted homogeneously together with Diphenylcarbonate in a steam-heated mixing container. This molten mixture is then taken up for the transesterification process.

To the expert it is clear that in this manner of handling of raw materials, a complete exclusion of Oxygen is technically not possible. On the surface and inside of the Bisphenol-A-crystals would always remain small traces of Oxygen.

On the other hand, it is seen that because of the high temperature during the transesterification process, the influence of Oxygen must be avoided at all costs.

Another objection to the use of crystallized Bisphenol A is moreover the disadvantage of having an additional step in the process. In addition, during the crystallization of Bisphenol A impurities, like for example metal traces, may impair the quality of the raw material.

These above mentioned defects finally lead to deficient constancy in the quality of the finished product, which reveals itself markedly in the characteristic yellowish colour of the Polycarbonate.

Since in the transesterification process there has to be a certain buffer capacity on the raw material side, direct loading with liquid Bisphenol A is excluded. In the high temperatures of more than 180^0 C, at which the molten Bisphenol has to be stored and handled because of the technological conditions of the process, during long storage periods a substantial quality reduction occurs because of the heat, which in turn permits production of only qualitatively inferior Polycarbonate.

The objective of the present invention is therefore a process for production of high-molecular aromatic Polycarbonate from Diphenylcarbonate and Bisphenol A according to the well known melting transesterification process, with or without the use of transesterification catalysts, which is distinguished thereby, that Diphenylcarbonate and Bisphenol A, which have as pure substances not yet fully changed their solid phase, are used together as molten mixtures in quantitative ratios by weight of between 30 : 70 and 70 :30, preferably between 45 : 55 and 55 : 45.

It was found surprisingly that one can avoid the above mentioned defects in raw material loading by using the molten mixtures prepared from Bisphenol A and Diphenylcarbonate according to the above ratios. A special and technically interesting variant in the process of this invention is the use of a molten mixture from 45 – 55 by weight of Bisphenol A and 55 – 45 by weight of Diphenylcarbonate, that is from somewhat equimolar quantities of both the components.

This molten mixture can be obtained for example by dosing of liquid Bisphenol, which directly emerges during Bisphenol production before its crystallization (compare DT-AS 1 168 445) into liquid Diphenylcarbonate. Besides the low melting point of only about 110^0 C, and the easier workability of the mixture at temperatures between 135^0 C and 155^0 C, this also shows surprisingly good colour stability. Since exclusion of Oxygen is possible to the maximum extent, such a processing of the raw materials in transesterification results in particularly bright-coloured products, which could not be produced so far. This result was unexpected, and can only be explained by pointing out that the molten mixture gains in colour stability by the addition of Diphenylcarbonate.

The advantage in the process claimed above is that the molten mixture can be prepared through the dosing pumps continuously as also discontinuously, whereby the production process can be varied according to the state of the technology.

The following description of the process is to be seen as only illustrative and not exclusive for production of such a molten mixture.

Diagram 1 shows this process schematically for production of a molten mixture of Bisphenol A and Diphenylcarbonate, as it has proved very useful in practice. For production and intermediate storage, there is a heated mixing container of a suitable size with a steadily maintained atmospheric cover of Nitrogen. The filling level varies

between a fixed minimum and a maximum level according to addition of the raw materials and removal of the molten mixture. The feeding in of liquid Bisphenol (BPA) and of the liquid Diphenylcarbonate (DC) is done by means of pumps, e.g.- gear-pumps or piston-pumps. An automatic control on the quantity fed in of the raw materials is ensured by the desired ratio between the two quantities. With the help of a centrifugal pump, the molten mixture can be taken out for condensation. The equipment is suited to continuous as also to discontinuous operation. One more variant worth mention is the production of the so called molten mixture with exact control on the mixing ratio of individual components with the help of static mixers, and moving it into storage containers of one's choice or even directly into the transesterification equipment.

The melting transesterification and polycondensation process under consideration in the present context for production of high-molecular aromatic Bisphenol-A-Polycarbonate is state-of-the-art technology. It involves transesterification of equimolar quantities of for example 2,2-Di-(p-hydroxyphenyl)-propane (Bisphenol A) with Diphenylcarbonate at temperatures between 50 and 350^0 C, preferably between 120 and 280^0 C, under atmospheric cover of an inert gas, and at a reduced pressure. As transesterification catalysts one may use basic transesterification catalysts like for example Sodium Methylate. The resulting molecular weight of the high-molecular Bisphenol-A-Polycarbonate can lie in between 25 000 and 36 000, and in general it is about 30 000. The relative solution viscosity (measured in Methylene Chloride, concentration = 0.5 g per 100 ml, temperature 25^0 C) of the received Bisphenol-A-Polycarbonate lies between 1.28 and 1.35.

The characteristic colour of the Bisphenol-A-Polycarbonate produced according to this invention is especially bright. The measurement of the Yellowness Index according to ASTM D 1925 gives values of 2.6. In comparison thereto lie the Yellowness-Index-Values of Bisphenol-A-Polycarbonates produced by other common molten mixtures between 5 and 6.

Example of Execution

A. A 10 m^3 container is equipped with a mixer, a device for steady maintenance of Nitrogenous atmosphere, and a heater coil.

The Bisphenol-A, after leaving the Bisphenol-A plant in liquid form is continuously poured into the mixing container at a temperature of $160\text{-}180^0$ C, and in a quantity of 300 kg/h (1.315 kMol). At the same time, molten Diphenylcarbonate from a storage container with 110^0 C is poured into the mixing container. The Diphenylcarbonate quantity amounts to 290 kg/h (1.355 kMol = 3 Mol-% excess). With continuous stirring the two components are mixed, and the temperature of the molten mixture amounts to $140\text{-}150^0$ C. The mixture has a characteristic colour of 5-10 units on the Hazen Colour-Scale, while from the characteristic colours of Diphenylcarbonate (5-15 Hazen) and Bisphenol-A (30-50 Hazen) a colour value of 20-35 Hazen would have been expected. (For Hazen Colour-Scale see ASTM D 1209/62).

B. 3 000 kg of this molten mixture are left in a transesterification equipment at a temperature of 150^0 C and are added to a high-molecular aromatic Polycarbonate, while adding also 5 g Sodium Methylate in a phenolic solution. The mixture is stirred for 7 hours, and when the pressure is gradually reduced from 100 to 1 Torr between $150\text{-}200^0$ C, the Phenol splits and is distilled. The resulting pre-condensate with a molecular weight of about 10 000, after being moved to a second reactor at 280^0 C and 0.3 Torr, is transformed into high-molecular Polycarbonate with splitting of more Phenol. With the help of gear-pumps the

glutinous molten Polycarbonate is taken out of the reactor and is drawn out in the form of cords with 3 mm diameter. After solidification and cooling of the cords, the latter are granulated. One gets 1640 kg (= 96.6% yield) of Polycarbonate with a mean relative solution viscosity of 1.312 (measured in CH_2Cl_2 at 25^0 C, concentration 0.5 g/100 ml) and an Yellowness-Index of 2.6 measured according to ASTM D 1925.

Comparative Example

In a 7 m^3 mixing container with a 15 bar steam heating 1475 kg (6.892 kMol = 3 Mol-% excess) Diphenylcarbonate and 1525 kg (6.688 kMol) crystallized Bisphenol-A are homogeneously melted together in a Nitrogenous atmosphere. One leaves this mixture in the transesterification equipment, adds 5 g of Sodium Methylate in a phenolic solution and proceeds further as described in Part B of the example above. One gets 1560 kg (= 95.1% yield) of Polycarbonate with a mean relative solution viscosity of 1.309 (measured in CH_2Cl_2 at 25^0 C, concentration 0.5 g/100 ml) and an Yellowness-Index of 5 measured according to ASTM D 1925.

Patent Claims

1. Process for production of high-molecular aromatic Polycarbonate from Diphenylcarbonate and Bisphenol A according to the well known melting transesterification process, distinguished thereby, that Diphenylcarbonate and Bisphenol A, which have as pure substances not yet fully changed their solid phase, are used together as molten mixtures in quantitative ratios by weight of between 30 : 70 and 70 :30.

2. Process according to Claim 1, distinguished thereby that Diphenylcarbonate and Bisphenol A are used together as molten mixtures in quantitative ratios between 45 : 55 and 55 : 45 by weight.

3. High-molecular aromatic Polycarbonates obtained according to Claims 1 and 2 above.

4. Molten mixtures in quantitative ratios from 70 – 30 by weight of Diphenylcarbonate and from 30 – 70 by weight of Bisphenol A, distinguished thereby, that Diphenylcarbonate and Bisphenol A as pure substances have not yet fully changed their solid phase.

5. Molten mixtures in quantitative ratios from 45 – 55 by weight of Bisphenol A and 55 – 45 by weight of Diphenylcarbonate, distinguished thereby, that Diphenylcarbonate and Bisphenol A as pure substances have not yet fully changed their solid phase.

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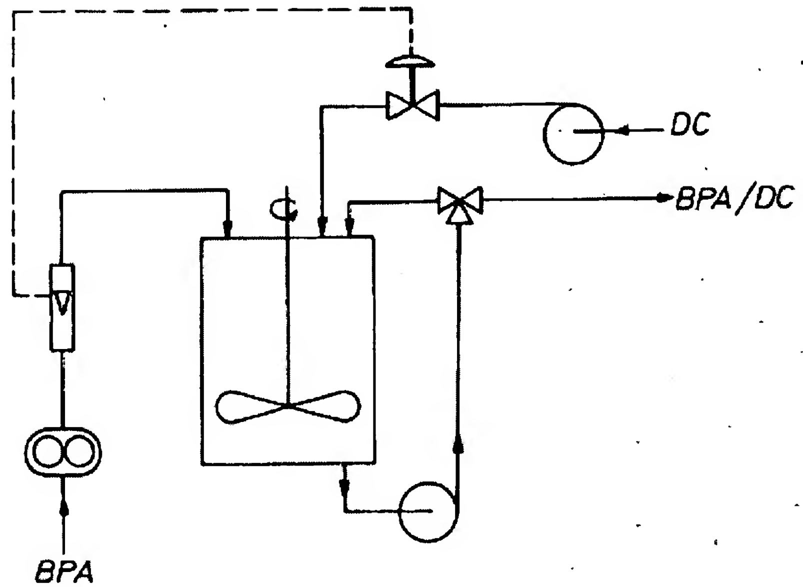
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